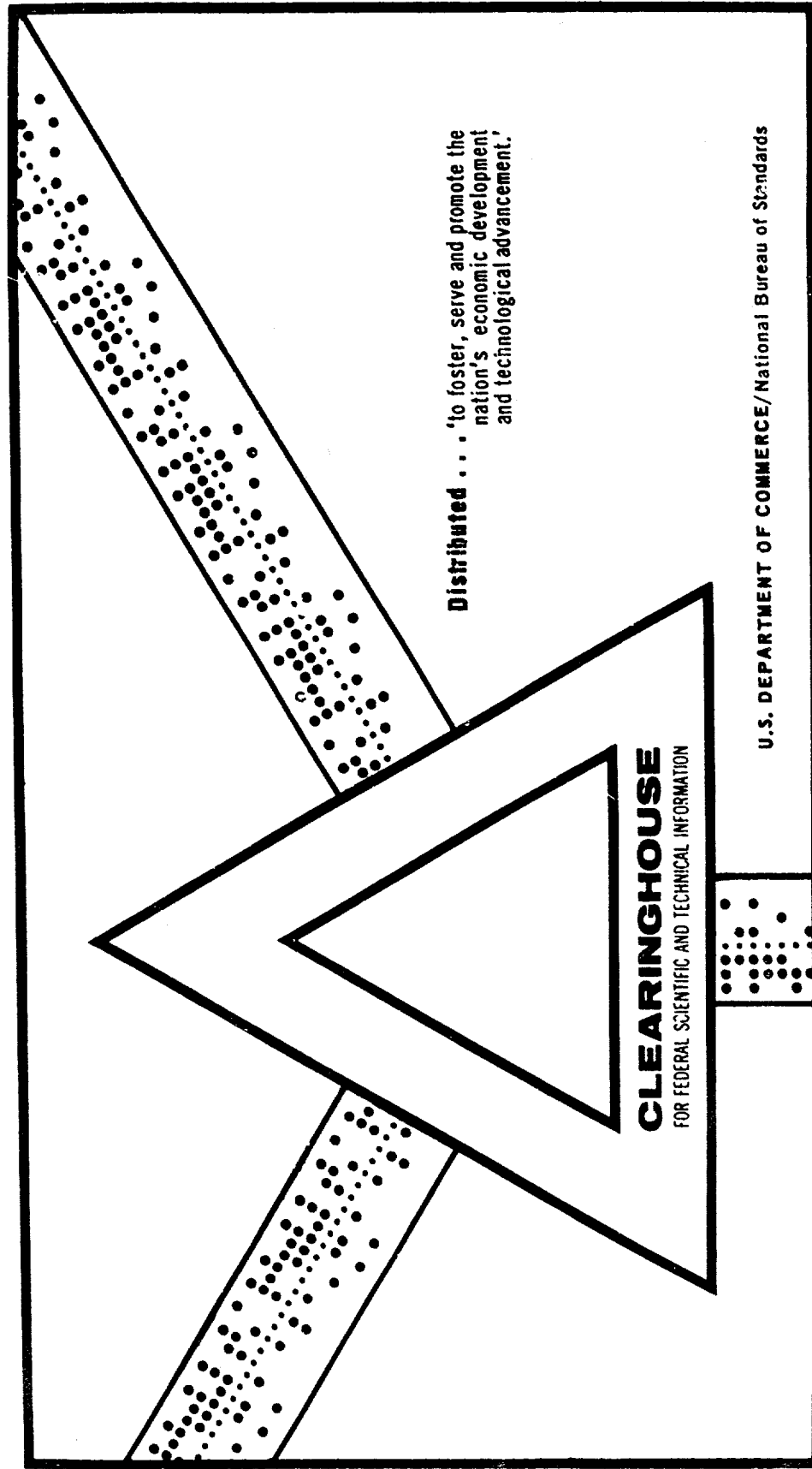PHYSICAL NATURE OF PROPELLANT SENSITIVITY

Ted A. Erikson

IIT Research Institute
Chicago, Illinois

30 November 1969

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Report No. IITRI-C6099-3
(Final Report)

PHYSICAL NATURE OF PROPELLANT SENSITIVITY

December 1, 1966 through November 30, 1969

Contract No. F44620-67-C-0036
IITRI Project C6099

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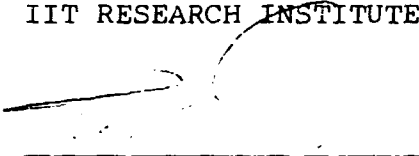Arlington, Virginia 22209

FOREWORD

This is Report No. IITRI-C6099-3 (Final Report) on IITRI Project C6099, Contract No. F44670-67-0036, entitled, "Physical Nature of Propellant Sensitivity." This report covers the period from December 1, 1966 through November 30, 1969.

Mr. Ted A. Erikson, Senior Chemist is the principal investigator. Dr. M. J. Klein, Director, Chemistry Research, Mr. C. K. Hersh, Assistant Director, Chemistry Research, Dr. I. J. Solomon, Senior Chemist, Mr. R. Remaly, Senior Engineer, Mr. Al Endres, Associate Engineer, Mr. Tom Stanley, Technical Assistant, Mr. W. A. Abel, Research Engineer, and Mr. A. J. Tulis, Associate Engineer have contributed to the project effort in various capacities.
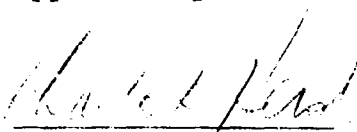
Data for this project are recorded in IITRI Logbooks C19670, C18417, C19233, and C18054.

Respectfully submitted,

IIT RESEARCH INSTITUTE

Ted A. Erikson
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Approved by:

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Assistant Director
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TAE/tp

ABSTRACT

PHYSICAL NATURE OF PROPELLANT SENSITIVITY

Interphase transformations have been studied with emphasis
on fundamentals and their relationship to problems that exist in
the explosive sensitivity of liquid propellants. Vaporization
and vapor-supply mechanisms play an important role in the sensi-
tivity of condensed-phase propellant systems but their quantitative
classification and assessment are difficult to realize.

A pseudo-thermodynamic vaporization coefficient, independent
of rate and equipment influence, has been evaluated for water and
introduced into the literature. Data for three other liquids,
carbon tetrachloride, chlorobenzene and butanol, have been statisti-
cally analyzed and results will be published. Consideration of
chemical reaction analogs of this treatment was limited.

A mechanism, namely, the fracture of a liquid system under
hydrostatic tensile forces is proposed by which liquid systems
can vaporize or supply vapor in an explosive fashion. Preliminary
verification of this mechanism for liquids in states of negative
pressure was obtained and supplemented by related experiments
with flashlamp heated gas-black surfaces in contact with both
inert and reactive liquids.

The status of the program is reviewed, and a list of accomplish-
ments and publications is given.

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PHYSICAL NATURE OF PROPELLANT SENSITIVITY

I. INTRODUCTION

The purpose of this program was to study and elucidate the mechanisms of phase change during a combustion process by using (1) revised principles of new approach[1] to steady-state thermodynamics and (2) kinetic characterizations of interphase transformations. The scope of this research was ultimately aimed at the problems associated with the meaningful ordering of propellant sensitivity or a more fundamental basis. The lack of practical control and/or understanding of explosive sensitivity still limits the utilization of newly developed and promising propellant materials in Air Force system applications.

The effort consisted of two phases; (1) the theoretical study of simultaneous chemical-reaction and vapor-supply mechanisms, with emphasis of the latter and (2) experimental work to assess vapor-supply mechanisms in the explosives process.

II. PROJECT STATUS

A. Mechanisms

Combustion is generally considered to be related to surface area. Therefore one hypothesis of this phase of the work can be

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[1]Tykodi, R. J., "Thermodynamics of Steady States." Macmillian Co., New York (1967).

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stated: "vaporization may be considered to be the rate-controlling step in certain propellant sensitivity problems." For this to be true, a mechanism that will generate vapor at explosive rates is a prerequisite for a sensitive propellant. Liquids in states of negative pressure, or hydrostatic tension, have received considerable attention but the difference between inter-molecular cohesive forces and intra-molecular adhesive forces is difficult to resolve. No substantial improvement over Tomlinson's views (circa 1870) is evident. Some history, definition, and character of states of negative pressure are discussed in detail in Appendix A.

For liquids in various states of negative pressure (equivalent to a superheat condition) the explosive nature of the vaporization process was experimentally demonstrated in two manners. First, some data that were obtained on a previous project were correlated with load cell records of the thrust that was developed. These records were shown to be directly related to the surface temperature of the "blackbody" absorber. These results are included in Appendix B, which is being re-submitted for publication.

Second, several experiments were performed with pure water and carbon tetrachloride liquid systems to measure the conditions that were required to nucleate bubbles at states of negative pressures. Summarizing these results, water tolerated around 170°C of superheat temperature at a negative pressure of -10 mm

Hg before bubble nucleation, the bulk of the water being held
at +10°C. Under similar conditions, carbon tetrachloride sur-
vived about 180°C of superheat temperature for bubble nucleation
on the _first_ attempt. This value decreased over about 6 subse-
quent trials to superheat temperatures about 75°C, which were
fairly reproducible thereon. This phenomena was repeated on 3
successive fresh batches of carbon tetrachloride. Unless liquid
passages were damped by a constriction, the vaporization was so
rapid that the glass equipment was demolished from the force of
the accelerating liquid columns. After bubbles were formed,
closures required about 10°C of supercooling and liquid column
vibrations were usually incurred. The value obtained for water,
170°C superheat at -10 mm Hg, is nearly 30°C higher than the
highest reported[2] superheat, namely, 288°F (142°C) at atmospheric
pressure.

The catastrophic acceleration of surface area formation for
liquids under negative pressure implies a mechanism by which an
unstable liquid propellant may supply vapor at explosive rates,
that is, condensed phase integrity is necessary to prevent
explosive runaway. The tolerance of states of negative pressure
is recommended as a simple measure of this integrity which can
be directly related to sensitivity.

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[2] Ibele, W., "Modern Developments in Heat Transfer," Academic
Press, New York, N.Y. (1963) p. 106.

B.   Vaporization

Based on a new application of thermodynamics to steady-rate
processes, the concept of migrational properties for the forced
vaporization of water has been introduced into the literature
as a result of this program. This method of ordering a vapor-
ization process was extended to three other liquids: butyl
alcohol, carbon tetrachloride and chlorobenzene. Data, obtained
from previous work, was statistically analyzed in an effort to
derive a mathematically tractable equation that substantiated
the results reported for by the averaged-graphical treatment[3]
that was published for water.

Considerable effort was expended to derive an analytical
expression of the data so as to extrapolate the limiting value
of a migrational property at equilibrium (zero mass flow) and
independent of equipment influence (infinite tube bore). In
equation form, the desired objective is

$$N = \lim_{\substack{n \to 0 \\ 1/r \to 0}} \left| \frac{\ln(P°/P)}{\dot{n}/A_s} \right| \tag{1}$$

where $\dot{n}$ is the mass flow, r is the circular tube radius, P° and
P are respectively the equilibrium and steady pressure, A_s is

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[3]Erikson, T. A. and Tykodi, R. J., Trans ASME, Jour Heat Trans.,
91, 221 (1969).

the surface area of the liquid and N is the desired migrational property.

Stepwise multiple regression analysis was performed on the three variable system; mass flow per unit tube area, logarithm of the equilibrium to steady pressure ratio and reciprocal tube radius, designated respectively as (z, x, y). Twenty equation forms were evaluated, the best fit being given by

$$z = a x + b x y + c x^2 \qquad (2)$$

The multiple correlation coefficient data for all 13 sets of data were generally better than 0.9 and in many cases better than 0.99. The desired endpoint that is indicated by Equation (1) (that is, the derivative of x with respect to z at $x = y = 0$) is simply the inverse of the coefficient, a, in Equation (2). Values of a were found to be quite sensitive, probably due to erratic convection influences as the experiments departed appreciably from equilibrium. A preliminary paper prepared for publication is contained in Appendix C with certain details of this aspect of the work.

Available time and funding did not allow study (by the steady-state thermodynamic approach[1] considered in this program) of the chemical-reaction counterpart of the vaporization scheme, namely,

$$T = \text{Limit} \quad \left[\frac{LN \ (K/Q)}{Z/V} \right] \qquad (3)$$

$$Z \longrightarrow 0$$

$$1/\gamma \longrightarrow 0$$

where Z is the reaction rate, V is the volume of the reaction zone, K is the equilibrium constant, Q is the activities of products and reactants at steady conditions away from equilibrium, and T is a "transformation" property.

The two properties, N and T, assume the same role for steady-rate processes that usual thermodynamic properties assume in equilibrium treatments. With their evaluation, definitions of sensitivity in a fundamental sense are anticipated because these properties are characteristic of rate processes conducted <u>at</u> equilibrium, and independent of equipment influnces. Perhaps the complications of collecting and analyzing appropriate data to evaluate such fundamental quantities is best circumvented by present-day engineering approaches in sensitivity problems, namely, trial and error.

III. BIBLIOGRAPHY

The following is a list of papers and talks that have been generated by research on this contract.

1. Erikson, T. A., Abel, W. A., and Remaly, R. R., "A Sensitivity Evaluation," AIAA Log No. J1587, talk presented at ICRPG/AIAA Solid Propulsion Conference, June 1967, Annaheim, Calif.

2. Erikson, T. A., and Tulis, A. J., "Shock-Tube Sensitivity Testing," talk presented at 5th Seminar on Sensitivity, May 9, 1967 Midwest Research Institute, Kansas City, Mo.

3. Erikson, T. A., and Tulis, A. J., "Flash Vaporization of Six Liquids by Flashlamp Heated Surface," revised paper to be re-submitted for publication (Appendix B).

4. Erikson, T. A., "Migrational Properties for the Steady Forced Vaporization of Water," talk presented at the Winter Annual Meeting, New York, N.Y., December 1-5, 1968 of the American Society of Mechanical Engineering.

5. Erikson, T. A., and Tykodi, R. J., "Migrational Properties for the Steady Forced Vaporization of Water," Trans ASME, Journal of Heat Transfer, 91, 221-8 (1969).

6. Erikson, T. A., and Tykodi, R. J., "Migrational Properties for the Steady Forced Vaporization of Several Liquids," being processed for publication submission (preliminary draft in Appendix C).

IV. RESULTS

A. Accomplishments

Portions of the accomplishments of this program have been summarized in a technical paper (No. 5, above), three talks (No. 1, 2 and 4, above), and three as yet unpublished papers (Appendix A, B and C).

Accomplishments of this program can be summarized as follows:

1. A survey of negative pressure phenomenon in liquids indicates several inter-related considerations dealing with adhesive-cohesive forces, specifically, galvanostalametry, tribonucleation and sonoluminescence (Appendix A).

2. The near-explosive nature of vaporization is indicated by load-cell records of liquids, both reactive and inert, in contact with flashlamp heated gas-black surface (Appendix B).

3. Migrational properties, independent of rate and equipment influences, have been introduced into the literature. Values of these properties are published for water and will be submitted for publication for three additional liquids (Appendix C).

4. Shock-tube sensitivity evaluations tend to differentiate the physical role of vaporization from the chemical role of reaction(s) in an explosively sensitive condensed-phase system.

5. Vaporization and vapor-supply mechanisms play an important role in sensitivity evaluations, for example, the fracture of a liquid system in hydrostatic tension generates vapor at sufficient rates as to be indistinguishable from an explosive-type response.

B. Additonal Information

1. Dr. Ralph J. Tykodi's book, "Thermodynamics of Steady States," Macmillan Co., New York (1967) provides a reference source for the basic ideas embodied in this study.

2. Picatinny Arsenal has requested permission from the American Chemical Society to reproduce the paper, "Crucial Pressure Index for Nitroglycerine Sensitivity," presented at the Division of Fuel Chemistry Meeting, April 4-9, 1965, Detroit, Mich.

3. At the 10th AFOSR Contractor's Meeting, September 4-5, Berkely, Calif., Dr. Harvey Michels of United Aircraft Research Laboratories, East Hartford, Conn., commented that the "migrational properties" introduced therein appears to be substantially similar, but of different form, to the reciprocal coefficients of Onsager's treatment. Verification would be of great value.

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V. SUMMARY

A propellant's "sensitivity" involves a complicated process during which it is difficult to assess the contribution from chemical reaction and vaporization or vapor-supply mechanisms. A "sensitivity" intends to sum up the result of slight additions of energy to an unstable, condensed-phase propellant system. In this research, the physical nature of propellant sensitivity was studied, namely, the classification of, and the mechanism(s) by which, changes in state complement the chemical reaction in an explosive process.

Two ideas were developed. First, pseudo-thermodynamic properties that are expected to be of use in classifying vapor-izability, independent of rate and equipment influences, were evaluated by analytical treatment of data that was obtained previously for several inert liquids. For the four liquids; water, carbon tetrachloride, chlorobenzene and n-butanol, limiting values of migrational coefficients for the steady forced vapor-ication process varied from 1.84 to 75.2 $\frac{sec-mm^2}{\mu-mole}$.

Second, several elements of liquid integrity were indicated by a limited study of liquid systems under negative pressure, that is, in a state of hydrostatic tension. A literature search was conducted that substantiates a proposed notion that the mechanism of fracture of adhesive-cohesive forces in a liquid can generate vapor at explosive rates, well above that required to sustain even a detonation. For flashlamp heated gas-black surfaces in contact

with both reactive and inert liquids near explosive responses were identifiable from load cell records. In experiments with liquids in states of negative pressures, superheat temperatures were above the highest reported, and fracture of the liquid system demolished the apparatus. Fast vaporization can be indistinguishable from an explosive-type response.

APPENDIX A

NEGATIVE PRESSURE

NEGATIVE PRESSURE

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ABSTRACT

NEGATIVE PRESSURE

Negative pressure is a term frequently cited in the literature. A limited literature search was conducted to unearth a better perspective for the origin, definition, and application of this term.

Historical origin is cited, theoretical definitions are developed from both thermodynamic and kinetic points of view, and three recent, unique experimental applications are briefly described. Some basic and applied needs for a clearer understanding of negative pressure, i.e., the cohesive forces of molecular interactions, are indicated in the discussion of limited applications.

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NEGATIVE PRESSURE

I. INTRODUCTION

The purpose of this paper is to give perspective and under-
standing to the term negative pressure. A cursory literature
search was conducted in Chemical Abstracts from 1957 through 1961,
1965 and 1966. Headings such as negative, internal, cohesive,
tensile, and surface pressures were used; and approximately 100
references were reviewed in an effort to unearth new developments.

Some historical evidence of negative pressure is cited and
a few of the more recent studies that involved this condition are
described in more detail. The mathematical origin of a negative
pressure is presented from two points of view. Several areas of
potential application and the profit evolved from a better under-
standing of the phenomenon are mentioned.

II. NEGATIVE-PRESSURE PHENOMENON

A. Experimental Behavior

Historical information about negative pressure is drawn
from a review published in 1941 (ref. 1) with more recent refer-
ences cited. The phenomenon that liquids maintain a state of
tension is fairly common, though not generally appreciated. The
most practical evidence of this phenomenon is the "sticking" that
sometimes occurs in creating a Toricellean vacuum by inverting a
completely-filled, closed tube of liquid such as mercury. Liq-
uid column heights well above a standard atmosphere, 760 mm Hg,

are easy to achieve in a clean system. The first measurement of such pressures was reported in 1843 when a sulfuric acid column was suspended 1.26 m above atmospheric pressure.

In 1850, through the measured values of thermal expansion coefficients, estimations of negative pressures were made by cooling small capillaries that were filled with bubble-free liquid. Negative pressures of the order of -100 atm were calculated before bubble nucleation, which causes the liquid to sharply crack into a reduced volume, occurred.

In 1882 open-end tubes that were filled with bubble-free liquid were spun in a centrifuge until centrifugal forces overcame the forces of negative pressure and released the liquid. From these first measurements negative pressures of -4.8 atm for H_2O were calculated. Measured values generally increased, for example, in 1950 a value of nearly -270 atm was reported (ref. 2) with water.

Plant transpiration, which carries the liquid to the top of tall trees, is a natural demonstration of these forces. In 1895 the top of an unbroken water column immersed in a mercury well was evaporated from a gypsum plate; 13 cm Hg was drawn up the column by tensile force. Eight years later under similar conditions -37.7 cm Hg was reported to be drawn up the column from a porous clay plate. More recent experimental (ref. 3) dealing with plants report measurements between 25 to 30 atm for cohesive forces.

B. Theoretical Discussion

The origin of a negative pressure is based on intermolecular forces where metastable, superheated states of the system can be generated under appropriate conditions. A liquid phase compromises the predominately attractive and repulsive forces of idealized solid-and gas-phase systems, respectively. Two methods are used to describe the concept of negative pressure. The first is conventional and describes the characteristics of the pressure-volume (P-V) diagram of a fluid with a typical thermodynamic equation of state. The second is perhaps less conventional but is believed to display a practical formulation of the phenomenon in terms of interfacial conditions.

1. Thermodynamic Considerations

The P-V diagram of a typical fluid (ref. 4) shown in Figure 1 displays the following characteristics. The mathematical relationship between pressure and volume approximates a rectangular hyperbola for isotherms above the critical temperature where the system is entirely in the vapor phase (right portions of Figure 1). The volume of the condensed phase barely changes pressure below critical temperatures (left side of Figure 1). The process proceeds isobarically as the condensed phase changes into vapor for any particular temperature (intermediate plateaus in Figure 1). Vapors can be supersaturated (DE and D'E') and liquids can be superheated (BC and B'C") while intermediate states of the system (CE and C"E') are physically unrealizable. At lower isotherms a negative pressure (C"C') arises by appropriate external conditions.

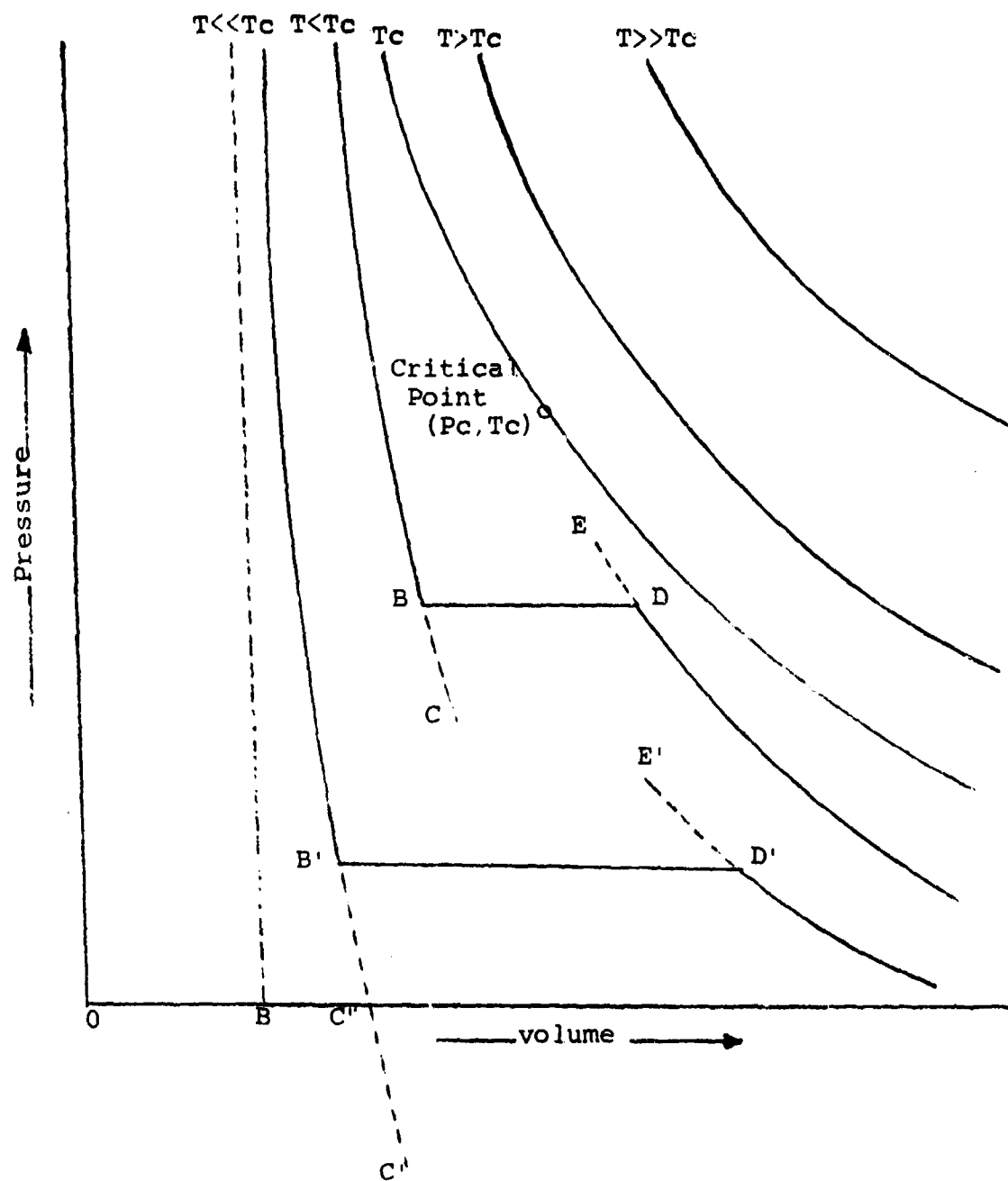The famous van der Waals equation makes a fair approximation of such representations:

Figure 1

PRESSURE-VOLUME DIAGRAM OF TYPICAL FLUIDS

$$(P + \frac{a}{V^2})(V - b) = RT \tag{1}$$

where

> a is a constant introduced to account for the
> cohesive forces between molecules

> b is a constant introduced to account for the
> covolume of molecules.

The term a/V^2 measures the internal pressure through a thermo-
dynamic analog by the first law as follows:

$$dE = TdS - PdV \tag{2}$$

and solving for P:

$$P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial E}{\partial V}\right)_T \tag{3}$$

by Maxwell's relationship:

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T \tag{4}$$

and:

$$P = \frac{\alpha}{\beta}T - \left(\frac{\partial E}{\partial V}\right)_T \tag{5}$$

where

> α is isothermal compressibility, $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

> β is isobaric coefficient of expansion, $-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$.

By rearranging Equation 1 and solving for P, the following equa-
tion is obtained:

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$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad (6)$$

A term by term comparison of this expression for P with Equation 5 shows that $\frac{\alpha}{\beta}T = \frac{RT}{V - b}$, the kinetic pressure and that $a/V^2 = \left(\frac{\partial E}{\partial V}\right)_T$, the internal pressure.

Since volume and temperature cannot be negative, negative external pressures arise when cohesive forces, $\frac{a}{V^2}$, can overcome the repulsive forces, $\frac{RT}{V - b}$.

2. Interfacial Conditions

Another way to look at negative pressure is to consider that the attractive and repulsive forces can reside in measurable liquid properties. (Ref. 4-8) The vapor pressure and the surface tension of a liquid are considered as quantities that are expressive of repulsive and attractive forces, respectively. At any liquid-vapor interface these quantities are profoundly affected by two primary factors, temperature and radius of curvature. The influence of temperature on the vapor pressure and surface tension is well known. The subtleties of the radius of curvature, however, are not generally appreciated.

Vapor-liquid surfaces in a liquid system can have both positive and negative radii of curvature that form bubbles and droplets, respectively. In this discussion bubbles and droplets, called pocks and pimples, respectively, imply different perspective, namely that any macroscopic surface within a liquid is simultaneously composed of both on a microscopic scale.

The fundamental and familiar capillarity equation:

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (7)$$
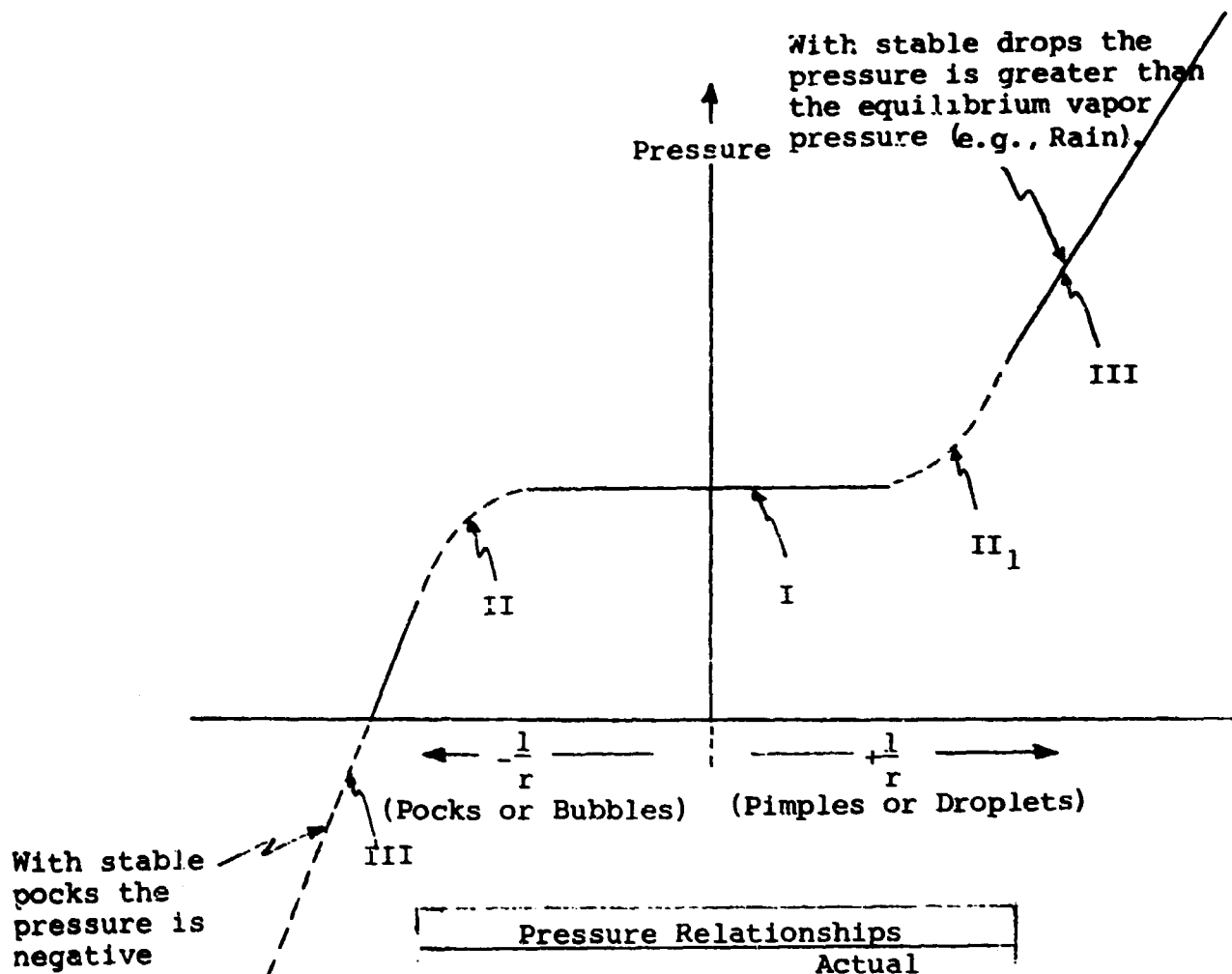
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which for a pure liquid system and for principal radii of curvature assumed to be equal (i.e., perfectly spherical rather than egg-shaped), can now be put into the form:

$$P = P^O + \frac{2\gamma}{r} \tag{8}$$

where P^O identifies the equilibrium vapor pressure of the liquid as usually reported.

Positive and negative radii of curvature are plotted in Figure 2 to correspond to pimples and pocks, respectively. Figure 2 lucidly shows negative pressure as well as the standard features of pressure variations. Considering the latter aspect, the measured pressure is equal to the usual equilibrium vapor pressure if P^O is sufficiently greater than the absolute value of $\frac{2\gamma}{r}$. The equilibrium vapor pressure is always referred to a relatively flat and planar surface ($\frac{1}{r} \longrightarrow 0$). The measured pressure approaches limiting values predicted by $P \longrightarrow \frac{2\gamma}{r}$ when the radii of curvature are smaller and have more pimpled or pocked characteristics. Values of the pressure are linear in $1/r$ as long as values of surface tension may be presumed to extrapolate to molecular dimensions.

Thus, microscopic pimples on macroscopic regions of liquid surface cause, locally, positive variations in the pressure relative to the equilibrium value. Equilibrium values of pressure are always temperature dependent so that variations can be made of nearly any magnitude by varying temperature. Similarly, micro- scopic pocks on macroscopic regions of a liquid surface or even

With stable drops the pressure is greater than the equilibrium vapor pressure (e.g., Rain).

Pressure

III

II₁

II

I

$-\dfrac{1}{r}$ (Pocks or Bubbles) $+\dfrac{1}{r}$ (Pimples or Droplets)

With stable pocks the pressure is negative

III

Pressure Relationships		
Region	Condition	Actual Pressure
I	$p^o > \left\lvert\dfrac{2\gamma}{r}\right\rvert$	$p \longrightarrow p^o$
II	$p^o \sim \dfrac{2\gamma}{r}$	$p = p^o + \dfrac{2\gamma}{r}$
III	$p^o < \dfrac{2\gamma}{r}$	$p \longrightarrow \dfrac{2\gamma}{r}$

Figure 2

DISPLAY OF CAPILLARITY EQUATION, $p = p^o + \dfrac{2\gamma}{r}$, FOR A PURE LIQUID-VAPOR SYSTEM

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within the liquid bulk (normally referred to as holes) can cause
local negative variations in pressure relative to equilibrium
values. Negative pressure values for a vapor cannot exist, but
pocks with sufficiently small radii can exist in the liquid bulk
(Ref. 5). Cohesive forces can prevail so that the experimental
phenomenon of negative pressure previously described is exempli-
fied.

In summary high temperature, small liquid radii of curvature
(pimples), and large radii of curvature (pocks) increase repul-
sive forces relative to attractive forces within a liquid so that
the liquid interfacial-area increases become very favorable.
Thus, vaporization is favored at any temperature for tiny pimples
(e.g., rain drops) and large pocks (e.g., ocean surfaces) and
increases with temperature. Or, negative pressure is favored at
low temperature, large pimples and small pocks, i.e., negligible
surface-to-volume ratios for the liquid.

C.   Special Cases

Some interesting experiments have been described in the lit-
erature under the negative pressure heading where certain conse-
quences of this state are used to identify and measure other quan-
tities that are not directly related. The contents of three most
recent references are briefly described in an effort to illustrate
typical approaches to the utilization of negative pressure.

1. Galvanostalametry

This technique evolved from early studies (ref. 9, 10) and
is presently being developed by the National Bureau of Standards

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to study certain electrochemical phenomena (ref. 11, 12). The
name, galvanostalametry derives from <u>galvano</u> meaning current and
<u>stalao</u>, a Greek word, meaning to drop. The general form of the
apparatus consists of a glass tube about 100 cm long and about
1 cm in diameter in which the column of liquid is suspended.
The upper end of the tube is fitted for electrodes, and appropriate
electrical equipment provides controlled current pulses.

The following characteristics have been observed: from the
conditions associated with the column drop (1) decomposition po-
tential of water is estimated by lowest applied voltage required
to drop column, (2) time required to drop the column at constant
current is proportional to ion concentrations, (3) current required
to drop column is proportional to area of electrode, regardless
of its shape, and (4) gas required to drop the column is formed
within 15 μsec after closing circuit. The last deduction is very
interesting; the hydrogen that is liberated by the 3×10^{-9} coulombs
of electricity to trigger the column drop is estimated to be equi-
valent to a volume of 6×10^{-10} cm^3 at S.T.P. or to a spherical
gas bubble with about a 8-μ diameter. The microscopic magnitude
of a disturbance to upset the metastable system should be obvious.

2. Tribonucleation

In this paper (ref. 13) several conditions connected with
tribonucleation (nucleation by rubbing) of liquids under hydro-
static tension, or negative pressure are reported. Water at 20°C
in a tension manometer at a negative pressure of 0.15 atm is re-
ported not to be disrupted by a 0.15-g-mercury droplet that is

impinged violently within the column head but is easily nucleated by a 0.1-g piece of soft silicone rubber that slides slightly. The results of this study generally substantiate that a metastable state of negative pressure is quite stable as long as no friction occurs between any two surfaces within the liquid. The conclusion that tribonucleation is not connected with any frictional heat flash (where local high temperatures are momentarily generated at asperities between rubbing surfaces) is based on experiments with materials of very low melting points.

The energy required to nucleate a bubble of critical size, 8μm, in these experiments, is estimated at 150 Mev from consideration of the changes in the free-energy function.

3. Sonoluminescence

Sonoluminescence (ref. 14) is a term that refers to the process of faint light emissions being generated by high-intensity sound fields. Positive and negative transient pressures are produced with a vibrator. The cavitation phenomenon depends upon several factors such as frequency, power levels, amplitudes and liquid properties.

A recent report on sonoluminescence concerns the dependency of sonoluminescence on static pressure (ref. 11). Studies are reported with equipment that delivers maximum acoustic power of 10 w at a fixed frequency of 21 kc/sec. This power is passed through a metallic stub in which energies of 9.5 to 32 w/cm^2 are achieved. A photomultiplier circuit is used to show that light output increases with increasing static pressure. The sonoluminescent efficiency, which is defined as the light output per unit

acoustic power (micro-amps/w), decreases with increasing static pressure and increases slightly at pressure levels of about 100 psia.

The mechanism of the process is not clearly defined, although it is obviously related to the adiabatic compression phenomenon that is involved with the collapse of small vapor cavities. Many studies of this type have been reported (ref. 15-17).

III. APPLICATIONS

Negative pressure arises in many applications of liquid systems. Some brief and unsophisticated discussions of selected areas, based on a cursory review of literature, are presented to give an appreciation of consequences of negative pressure.

A. Cavitation

Cavitation is simply the result of various processes in which kinetic energy is added to move slugs of liquids in such directions that the generated forces overcome the tolerable negative pressure. Pocks, or holes, are formed that can cause upon collapse intense and local points of energy. An early study (ref. 8) formulates the pressure than can be developed as functions of the rate of collapse, and recent studies (ref. 15-17 19,20) report observations during collapse such as (1) recorded light flashes of less than $5\mu sec$, (2) pressures from transducer records estimated from 10^4 to 10^5 atm, (3) pulsation of gas bubbles breaking up the surface of the liquid, and (4) cavitation and bubble formation may be different

processes. Under such conditions it is not unlikely that chemical bonds are broken, and indeed, the pitting of propeller blades and the initiation of explosions originate from cavitation and bubble collapse.

Various operations can produce cavitation; examples are fluid pumping, fast-closing valves on moving fluids, fluid mixing, ships propellers, pressure pulsations, sonic waves, and like situations where the interplay of kinetic energy and inertia can disrupt cohesion and adhesion (ref. 21-23). Sonic generators (ref. 17) produce cavitation on a microscopic scale. Most studies that attack this problem from the practical point of view attempt to evaluate the effects of (1) additives to vary surface tension forces and (2) materials to vary adhesive forces. The object of such studies is to extend the limits of handling operations from which cavitation, causing operational damage, may evolve.

B.   Gravitational Influences

One investigator (ref. 24) pointed out that about 1700 Newton (ref. 25,26) distinguished between gravitational and molecular cohesive forces. In 1911, Mills (ref. 27) compared chemical, molecular, gravitational, electrical, and magnetic fields of action and concluded that all forces can become apparent only at a surface. He quoted a Smithsonian Report of 1876 in which gravitational attractions were estimated to propagate with velocities at least 50×10^6 times greater than the speed of light. Several studies (ref. 28 29) since concern themselves with gravity waves and interactions in colloidal suspensions, coagulation and floculation.

Recent studies (ref. 30,31,32) are apparently resurrecting the interactions of gravity waves by using mathematically complex formulations that are difficult to understand.

Nevertheless, it should be perfectly obvious that rates of mass alteration in a system can be induced by several fields of action that probably interact simultaneously. In a dynamic process, this interaction on a microscopic level, such as molecule-system, can only be ascertained by extrapolation from measurements that were made on a macroscopic level, such as, surroundings-system. Obviously with mass alteration at a surface the inter- and intragravitational influences are complicated. Sizing is very important. In earth's gravitational field, a small drop of mercury on a bench top is nearly a perfect sphere, whereas under more intense gravitational forces it approximates a flat plate.

At a limiting state of negative pressure, the cohesive forces that maintain integrity of the system are just able to balance the repulsive forces that, once triggered, disrupt the system. The possibility of understanding any means for an anti-gravity device requires a thorough appreciation of these forces.

C.   Point Nucleation

The statistics on bubble and droplet growth and decay are very mathematically involved. (e.g. ref. 33). Larson estimated (ref. 34) that only 1 molecule is required to nucleate boiling in a liquid. The origin of the 1 molecule requires the energy to be of the order that can be liberated by breaking a chemical bond. The chemical nature of phase transformations has always

been elaborated upon and suggests that nucleation may originate from bond rupture. Although the idea of phase transformations having a chemical nature is plausible, the proof is practically impossible because of the microscopic inadequacy of any monitoring device.

In a state of negative pressure, the initiation of many processes (e.g., galvanostalametry and tribonucleation) approaches microscopic levels. Presumably as one approaches higher and higher degrees of cleanliness and negative pressure investigation of phenomena is possible on a near-microscopic basis. The occurence of particular phenomena is identified by the macroscopic release of the column.

D.   Surroundings

The study of droplets and bubbles form the central issue in phase transformations. There is, however, an area and volume interplay with the surroundings such that when a droplet or bubble nucleates, and grows from a central point, there is depletion of the surroundings from a distal origin. The amount of surroundings in the form of vapor for droplet growth, and liquid for bubble growth, need not be arbitrary. Further, droplets and bubbles can be sufficiently microscopic to barely affect the properties of the surroundings.

An interesting study of such an inverse approach to droplet and bubble stability was reported (ref. 35) wherein the mass transfer between two liquid surfaces across a spherical _air_ shell was studied rather than the mass depletion that usually occurs

from the normal soap-type bubble. The disparity of interest is unusual; rather than studying the growth (or decay) of a vapor bubble within a spherical liquid shell, the attention was directed to the growth of a liquid droplet within a spherical air-vapor shell.

IV. SUMMARY AND CONCLUSIONS

The cohesive forces of a liquid, which determine the practical limits of negative pressure to which it can be subjected, are theoretically quite high. Any process in which negative pressures can be experienced establishes a metastable state of a liquid system on a nearly permanent time basis. In this state, certain considerations are involved to upset the metastable condition. Once the condition is upset, several concommitant transformations of phase, surface area, volume, velocity, pressure, and temperature rapidly occurs. The growth in radial distance of any phenomenon nucleating at a point causes geometric reverses, i.e., crossovers in volume and surface so that energy activation and energy release, which are presumably interdependent in the growth stage of any process, invert and/or oscillate with time.

A concise understanding of the contributions due to all factors in any process is necessary. To my knowledge the problem of molecular surface interaction is reasonably summarized by Tomlinson in two papers published about 1870 (ref. 36,37). He describes in great detail the consequences of "active" and "passive" surfaces for many materials of practical interest, the physical and

chemical effects connected with the adhesive forces, and various influences of cleaning methods. "Clean surfaces do not nucleate bubbles" summarizes these papers. Through the last 100 yrs the understanding of molecular surface interactions is being "cleaned up" but it is only a difference in degree, not in kind. The cohesive forces of pure liquids are still an elusive property of matter that can only be approached by measurements of the surroundings which always tend to interact with the phenomenon being studied and influence the result.

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APPENDIX B

FLASH VAPORIZATION OF SIX LIQUIDS
BY FLASHLAMP HEATED SURFACE

FLASH VAPORIZATION OF SIX LIQUIDS BY FLASHLAMP HEATED SURFACE

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ABSTRACT

Small quantities of liquids that are in contact with a flash lamp-heated gas-black surface generate characteristic pressure responses. Load-cell records are used to identify induction times from 65 to 440 μsec and measurements that are proportional to vaporization rates for the liquids methanol, water, n-butanol, ethylene glycol, nitroglycerine, and glycerol, increasing in that order. The surface temperature of a flash-heated gas-black adsorber with respect to time can be calibrated by this technique.

INTRODUCTION

This paper reports the results of initial experiments that, to the best of our knowledge, represent a new method for characterizing (1) induction times to flash vaporization, (2) relative vaporization rates for liquids under such conditions, and (3) surface temperatures of rapidly heated gas-black. These data are a result of vaporization and explosive sensitivity studies on the ambiguous nature of the chemical reaction and phase change that occur during the combustion of solid and liquid propellants and explosives.

To place this paper in its proper perspective, certain aspects of the vaporization and the reaction of condensed phases under fast-heating conditions are briefly discussed. For vaporization, a liquid must accumulate some degree of temperature excess above the saturation temperature that corresponds to the external pressure. In terms of heat transfer (ref 1,2), various degrees of superheating are recognized as the driving force for the several defined regimes of vaporization, or boiling. These regimes range from natural convection through nucleate boiling to film-type boiling. The latter is nearly explosive and occurs near the boiling temperature at the external pressure. In film-type boiling, the temperature of the heating surface can increase rapidly. Heat transfer by conduction and radiation then predominate through an insulating vapor film.

For reaction, a chemical species must accumulate some degree of temperature excess (energy) for decomposition. Under given

conditions, decomposition temperatures can be reported, but the results of isothermal experiments are usually (ref. 3) converted into the temperature coefficient for the reaction, i.e., the activation energy. When the exothermic nature of the reaction reaches a sufficient level, self-heating begins and explosion results.

In explosive sensitivity evaluations, the separation of the related nature (explosion) of these two processes poses a dilemma. Both processes exhibit a temperature runaway; for vaporization, the heating surface, and for reaction, the material. Both processes are related to the rapidly rising temperature of a heated surface. For an unstable liquid, the formation of a vapor-liquid interface (bubbles) or nucleate boiling must be critical, since further temperature excess of the surface probably activates the explosion. Thus our interest in vaporization is acute.

Small liquid samples were placed in direct contact with a gas-black surface, which was then rapidly heated by means of a high-intensity-flash lamp. Load-cell records of the explosive thrust that developed are reported for six liquids; five of these are relatively inert (methanol, water, n-butanol, ethylene glycol, and glycerol) and the sixth is reactive (nitroglycerine). The experimental procedure is described, and the results are presented and discussed.

EXPERIMENTAL PROCEDURE

Figure 1 is a schematic of the experimental apparatus. The source of irradiation was a commercial[*] xenon-filled flash tube, rated at 4000 joules at 4000 volts. It is an Edgerton-type lamp that consists of a 4-1/2 turn coil of quartz tubing approximately 1-1/2-in. in diameter and 2 in. long. The tube was placed in a 9-in. diameter polished hemispherical aluminum reflector to semicolumnate the radiant energy.

The discharge energy was supplied from a variable bank of five 100 ufd capacitors rated at 4000 volts. The capacitors were charged through a current-limiting resistor by a continuously variable 0-10 kilovolt power supply rated for 5 ma output. A Thordarson type 22R44 photoflash transformer rated for 15 kilovolt peak output supplied the ionization potential which composed the triggering mechanism for the flash discharge. Voltage across the flash-tube electrodes was monitored by an attenuated signal from a 1000:1 resistive voltage divider. This voltage monitor also supplied a trigger signal for the scope sweep circuit at moment of discharge.

The characteristics of the light output were monitored with an RCA 931-A photomultiplier sensor, which has a flat response from 0.3 to over 0.5 μ, with attenuation of 100 at 0.65 μ. Because of the tube's extreme sensitivity, an adjustable pinhole aperture was used with reflectors and trial and error placement until response without saturation was obtained. The output

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[*] Kemlite Laboratories, Inc., Chicago, Ill.

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signal of the photomultiplier was directly monitored through appropriate amplifiers on a Tektronix 545 oscilloscope, and photographic records of the trace were made with a Polaroid land camera. The circuit rise time was about 1 μsec.

Two representative oscillograms with light and load-cell (discussed later) outputs are displayed in Figure 2 for a blank test (no liquid) and for a test with two drops of nitroglycerine on a gas-black surface. In both tests, the flash tube was fired at 4200 volts; the falling voltage triggered the trace. For records 2a and 2b, the capacitance was increased from 100 to 200 μfd to demonstrate that light duration increased; i.e., the RC time constant for the circuit was doubled, although the light intensity remained constant since it had been fixed by the firing voltage. For the blank test, no load-cell output was obtained; however, the nitroglycerine in record 2b developed a positive thrust (explosion, as evidenced by glass pulverization, also) at about 270 μsec from the moment of oscilloscope triggering.

The radiant energy was converted to thermal energy by absorption upon a gas-black surface, which was prepared as follows. Precleaned microscope slides, 25 x 75 x about 1 mm, were traversed across the tip of a natural gas flame until an opaque film of gas carbon was uniformly deposited. From other tests, it was found that the thickness and uniformity of the carbon-deposited surface was not critical if a sufficiently thick (opaque) film was established.

The prepared plate was placed directly on the surface of a Kistler[*] type 910 quartz load cell, with the gas-black surface facing up and located approximately 8-in. below the reflector rim. About two drops of a test liquid was placed directly upon the surface of the gas-black. A series of tests was conducted at the identical discharge of 4000 joules; the oscilloscope sweep was triggered by the minus-going (upon discharge) signal from the discharge voltage, which was attenuated by about 1000 with a voltage-divider system, as discussed earlier.

Figure 3 shows the oscillograms for the load-cell response under these conditions for the following six liquids: (a) methanol, (b) water, (c) n-butyl alcohol, (d) nitroglycerine, (e) ethylene glycol, and (f) glycerol. All sweeps were at 50 μsec/cm. The records are characterized by an induction time, as determined by the time at which a positive force (increasing downward) occurs, and a slope of the force-time record, estimated from the original photographs. The character of a record with an explosive material such as nitroglycerine is distinctly different.

RESULTS AND DISCUSSION

As shown in Figure 3, the numerical values of induction time and the average rate of deflection (force) were evaluated. The numerical results for the six liquids are summarized in

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[*]Kistler Instrument Co., Clarence, New York.

Table 1. The deflection rate for nitroglycerine could not be estimated because of its sharp explosive nature. As an experimental aside, it can be said that the glass microscope slides were always recoverable with inert liquids, whereas the slides were completely pulverized in nitroglycerine tests. Also included in Table 1 are the boiling point temperatures at 1 atm for the liquids because of their use as a reference point

The temperature of the gas-black surface can be assumed to increase as if the surroundings were absent; i.e., the heating is practically adiabatic because of the short time duration of the experiment. As the surface temperature crosses the boiling point temperature for the liquid under test, nucleate-to-film boiling occurs, and thrust due to the rapid flash vaporization process is imparted to the load cell. The induction time for the appearance of this thrust can be related to each liquid's boiling point as shown in Figure 4. In fact, this reasoning suggests a method for calibrating the gas-black surface temperature variation with respect to time in a given physical arrangement and light flash By extrapolating the measured induction time data to room temperature, approximately 50 _sec elapsed from the moment of oscilloscope trigger to the moment of pickup of mechanical response. This is comparable to the 50 _sec for a buildup of about 75% of maximum photocell response, as shown in Figure 2

That this reasoning is valid is further supported by reasonable agreement between two methods that were employed to

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estimate proportional rates of vapor production during transient
heating. First, the vaporization rate can be roughly represented
by the rate of deflection (force) of the load-cell records, where
a constant amount of liquid is assumed. These slopes, as estimated
from the original records shown in Figure 3, are listed in Table 1.
Second, the rate of vaporization is also directly proportional
to the heat transfer rate, which increases with increasing
temperature of the gas-black surface. These increases in heat
transfer rate can be estimated by using the data in Table 1 to
form the ratio of the difference between the transient surface
temperature of the gas-black and the initial (bulk) temperature
and the induction time (corrected for the 50-μsec time lapse
mentioned previously). The proportionality factors for both of
these estimates are combined by forming the ratio for each of
the liquids. These ratios, as shown in Table 1, average to about
31 °C/div within about 15% for the five liquids that gave
measurable data.

CONCLUSIONS

The unique experimental arrangement and technique that is
described exhibits promise for characterizing the flash vaporization
even combined with reaction, process for liquids. Small liquid
samples were placed in direct contact with a prepared gas-black
or blackbody surface. This surface was rapidly heated by
absorbing the radiant energy delivered by a high-intensity flash
lamp.

The key in these experiments was the direct measurement of the thrust from vaporization. The preliminary results showed direct load-cell records of the thrust from the sample-surface combination when exposed to high-intensity-flash light. The records can be used to derive induction times to the development of force and relative measurements of vaporization by the rates of change of the force. When induction times are related to the boiling point (at 1 atm) of the test liquids, the smooth curve that results defines the temperature-time history of the gas-black surface. Flash (film-boiling) vaporization must develop the thrust which is believed to begin sufficiently near the boiling point temperature.

Vaporization rates, as estimated from (1) rates of force and (2) rates of change in heat transfer, (estimated by average, temperature difference) agree within about 15% and confirm the analysis of the events that transpire.

Further studies are now in progress to evaluate the physical and the chemical effects that occur with other (1) types of radiant energy converters, (2) reactive liquids, (3) levels of external pressure, and (4) initial temperatures.

ACKNOWLEDGMENTS

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Office of Aerospace Research, a re-treatment of the data was
performed.

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TABLE I – SUMMARY OF RESULTS FOR SIX LIQUIDS IN CONTACT
WITH FLASHLAMP HEATED GAS-BLACK SURFACE

Test Liquid	Liquid Boiling Point (1 atm), °C	Measured[a] Induction Time, µsec	Deflection[b] (Force) Rate, Div/µsec	Average Rate[c] of Temperature Rise °C/µsec	Ratio,[d] °C/Div
Methanol	65	65	0.12	2.9	24
Water	100	80	0.071	2.6	36
N-butanol	118	95	0.054	2.1	39
Ethylene glycol	197	220	0.035	1.0	29
Nitroglycerine	206(est)	260	>1	0.87	–
Glycerol	291	440	0.024	0.69	29

[a]Oscilloscope triggered by voltage drop in flashlamp circuit.

[b]Estimated slope of force-time records in Figure 3.

[c]Difference of boiling point and initial (25°C) temperature divided by corrected induction time.

[d]Ratio of c to b; vaporization rates estimated from heat transfer and thrust, respectively.

LIST OF FIGURE TITLES
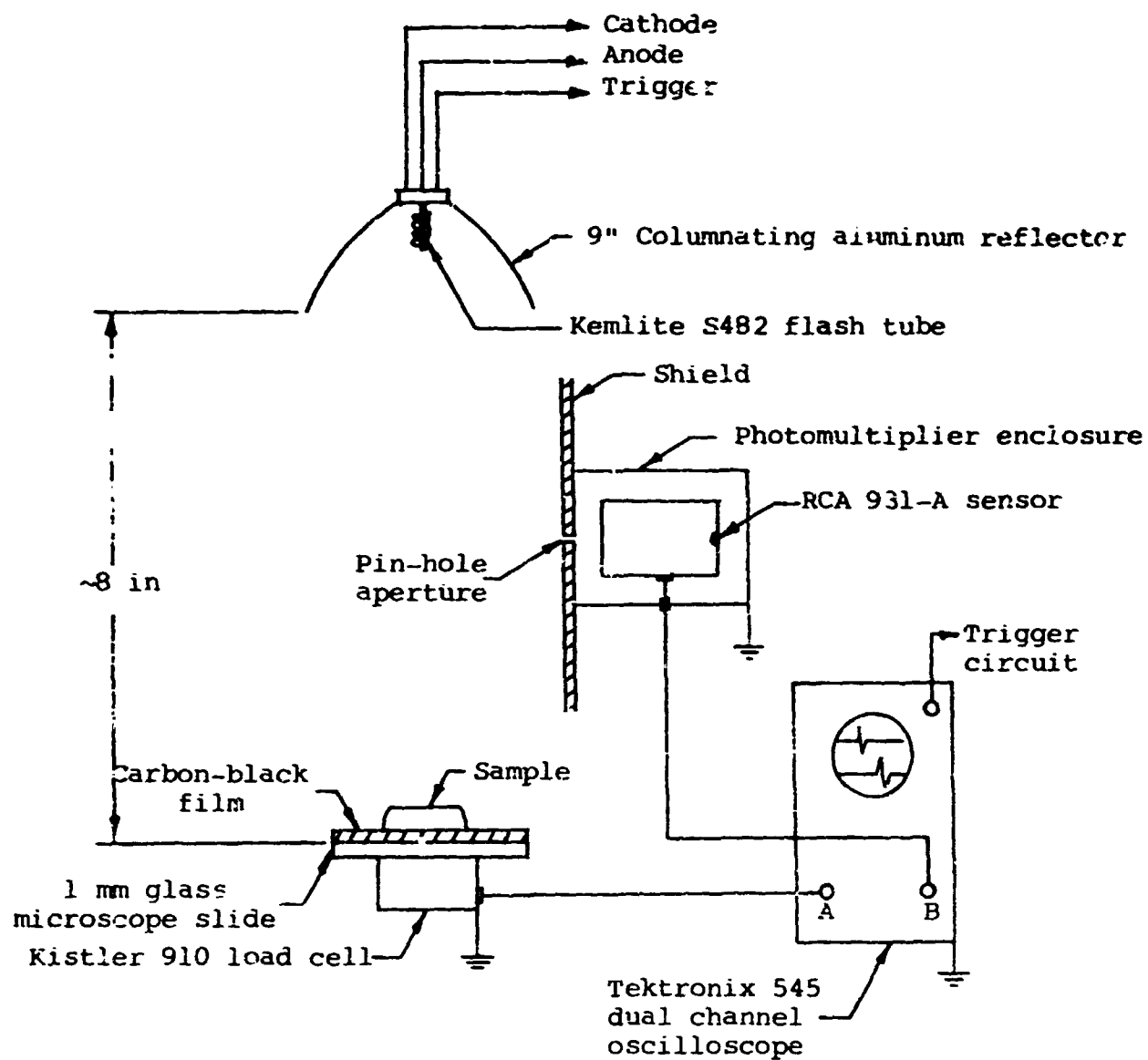
Figure

Figure 1. EXPERIMENTAL SET-UP
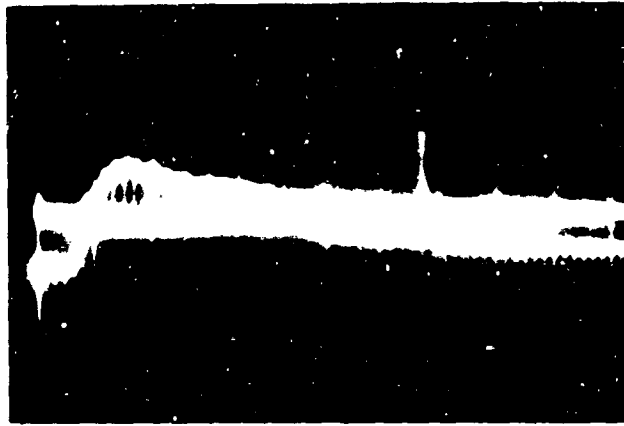
(A) Blank, 4200 volts and 100 μfd
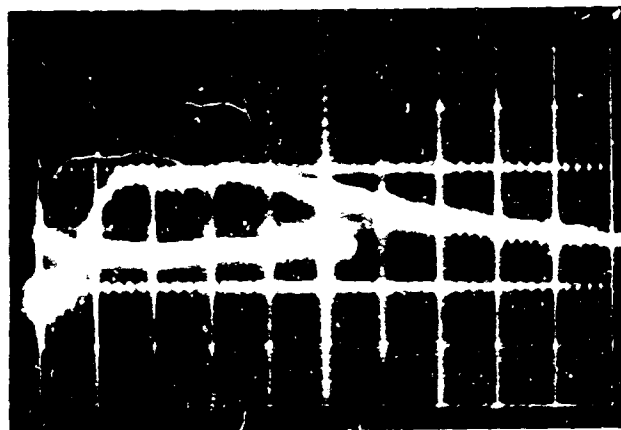
(B) Nitroglycerine, 4200 volts and 200 μfd

Note: All sweeps from left to right at 50 μsec/cm. Dashed and solid traces are photomultiplier and load cell outputs, respectively.

Figure 2. PHOTOMULTIPLIER-LOAD CELL RECORDS
OF FLASHLAMP HEATED GAS-BLACK SURFACE

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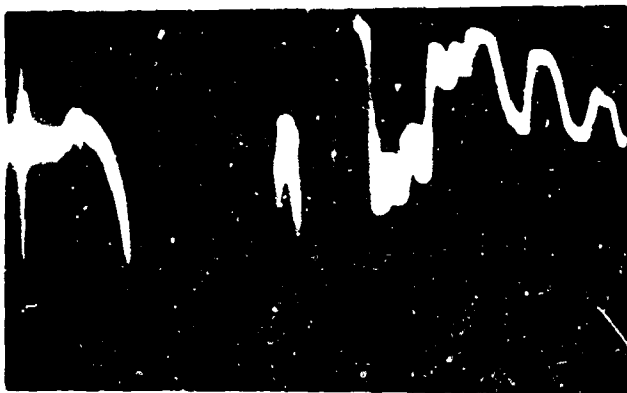
(A) Methanol
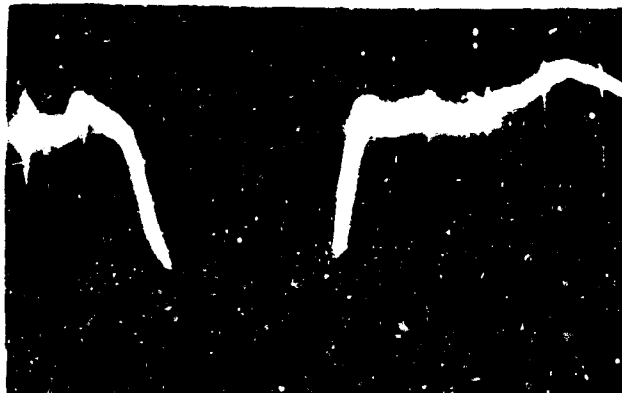
(B) Water
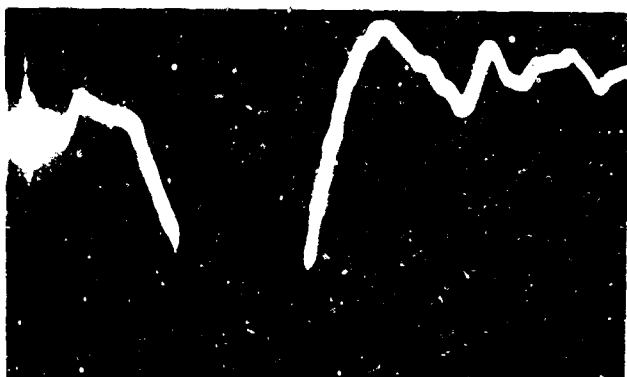
(C) N-Butyl Alcohol

(D) Nitroglycerine

(E) Ethylene Glycol

(F) Glycerol

Note: All sweeps from left to right at $50\,\mu\mathrm{sec/cm}$ with force increasing downward.

Figure 3. LOAD CELL RESPONSE FOR SIX LIQUIDS
BY FLASHLAMP HEATED SURFACE
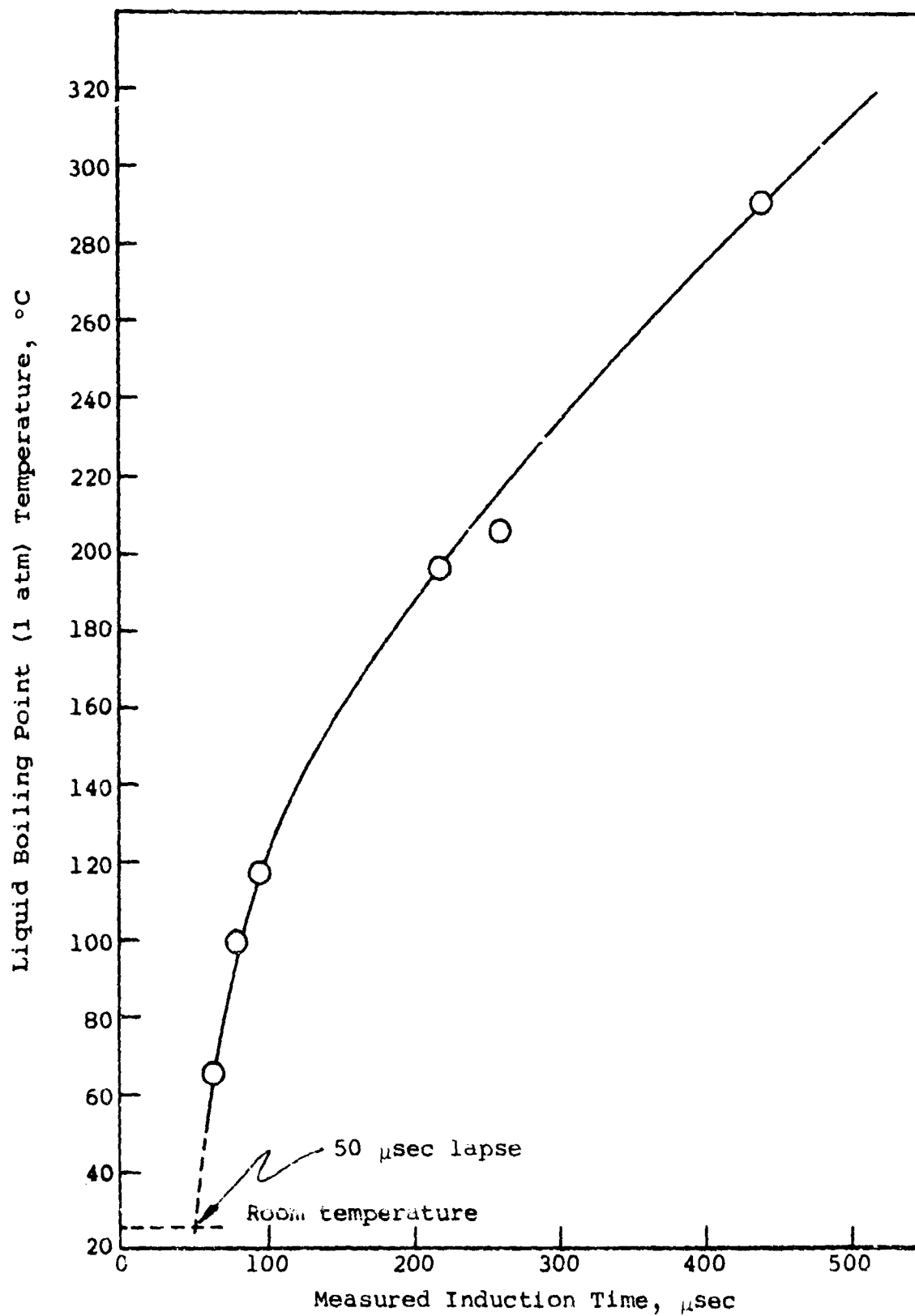
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Figure 4. BOILING POINT TEMPERATURE RELATION
WITH MEASURED TIME LAPSE FOR PICK-UP OF VAPORIZATION THRUST

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APPENDIX C

MIGRATIONAL PROPERTIES
FOR THE STEADY FORCED VAPORIZATION OF LIQUIDS

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LIST OF TABLES AND FIGURES

MIGRATIONAL PROPERTIES
FOR THE STEADY FORCED VAPORIZATION OF LIQUIDS

I.   INTRODUCTION

A new treatment of thermodynamics[1-2] has been introduced
into the literature to describe certain aspects of steady-rate
processes. Classical principles are used, assumming that terminal
parts and gradient parts can be defined with uniform and time-
invariant properties, respectively, in a closed system where a
steady non-equilibrium process is maintained. This approach has
a different flavor than usual non-equilibrium thermodynamics[3-6]
because a sequence of steady states away from equilibrium are
proposed (and believed) to define values of a property that
describes the particular process in question in an equilibrium
state. Thus, measured values of a derived coefficient for a
non-equilibrium, but steady, process are extrapolated to the
non-measuraable, equilibrium state in a procedure that is not
unlike the methods[7] that have been developed to evaluate the
limiting equivalent conductance of a solute in a solvent at
infinite dilution.

This paper is part of a series to accomplish two purposes.
First, a collection of new data for liquids in steady forced
vaporization are reported, taken so as to meet certain requirements
of steady state processes as defined by the aforementioned approach.
Such data have been heretofore generally unavailable. Second, a
limiting value of a process coefficient at the condition of

equilibrium and independent of the equipment influence is evaluated from said date. Procedures are described so that the coefficient assumes the character of a property of the material for the process in question. Thus, values of this coefficient that are derived from several steadily maintained conditions away from equilibrium state and infinite tube bore. In equation form, the desired endpoint is

$$N = \text{Limit} \quad \left[\frac{\text{Ln } (P^\circ/P)}{\dot{n}/A_s} \right] \qquad (1)$$
$$\dot{n} \longrightarrow 0$$
$$1/r \longrightarrow 0$$

where the two conditions, $\dot{n} \longrightarrow 0$ and $1/r \longrightarrow 0$, define the limiting value of N to be approached by extrapolation of a sequence of steady states near equilibrium.

II. EXPERIMENTAL WORK

The equipment is described elsewhere.[8] Briefly, liquids were vaporized from five precision-bore glass tubes (identified A through E) varying cross-sectional area from 11.28 to 285.00 mm^2. The apparatus was immersed in a 10-gallon water bath equipped with a high speed stirrer and thermostatically controlled to better than $\pm$ 0.1 deg C. The fixed temperature of the bath was used as the monothermal reference point for the process. Liquid levels and heights were measured with a Gaertner Model 908 cathetometer which has a scale resolution of $\pm$ 0.5 mm. Liquids were thoroughly degassed and leveled to an appropriate position in the equipment.

Changes in liquid level height with respect to time at several levels of pressure and three selected temperatures were used to give measurements of the steady mass flow.

The data collected from experiments on water were reported previously.[8] Data for three other liquids, carbon tetrachloride, chlorobenzene and n-butanol, are presented in Tables 1, 2, and 3, respectively. Therein are tabulated the steady mass flow that was measured for each of the five glass tubes at corresponding pressures and the three selected bath temperatures. At any given bath temperature, the tables indicate in general, that the steady mass flow monotonically increases with (1) lower than equilibrium and steadily maintained pressure above the liquid surface and (2) larger bore tubes.

III. GENERAL CONSIDERATIONS

Complications in data handling and appropriate extrapolative techniques arose. As a first approximation, a linear fit (plot) of Ln P as a function of $\dot{n}$ correlates the measured data with good results as reported elsewhere[1,8] provided conditions are generally near equilibrium. For the best analytical fit by least squares analysis, the intercept of such a plot at $\dot{n} = 0$ does not generally co-incide with the equilibrium value of the vapor pressure for the particular bath temperature that is involved. Thus to obtain a limiting value of the slope, N, as $\dot{n} \longrightarrow 0$ (i.e.,) $P \longrightarrow P^\circ$) requires major corrections unless data are taken sufficiently near equilibrium. For example, note that the 2°C carbon

Table 1

DATA FROM FORCED VAPORIZATION OF CARBON TETRACHLORIDE

Pressure (P), mm Hg	Deviation,[a] mm Hg	Temp. (T), °C	Mass Flow ($\dot{n}$), μmoles/sec				
			Tube A	Tube B	Tube C	Tube D	Tube E
314.93	0.27	50.0	0	0	0	0	0
299.92	0.46	50.0	0.566	1.03	1.63	2.31	4.18
289.72	0.44	50.0	1.01	1.90	3.17	4.70	8.95
278.52	0.31	50.0	1.40	2.74	4.48	6.85	12.7
268.29	0.14	50.0	1.77	3.51	5.95	8.88	17.3
258.05	0.11	50.0	2.28	4.42	7.60	11.5	20.7
227.23	0.10	50.0	3.61	7.22	12.95	18.2	36.85
113.73	0.40	25.0	0	0	0	0	0
110.85	0.19	25.0	0.262	0.483	0.755	0.962	1.62
104.70	0.10	25.0	0.745	1.40	2.21	3.13	4.89
102.35	0.10	25.0	1.32	1.73	2.89	4.14	6.96
91.66	0.09	25.0	1.81	3.55	5.91	8.66	15.2
82.46	0.4	25.0	2.32	4.75	8.59	13.3	18.4
34.92	0.12	2.0	0	0	0	0	0
29.91	0.22	2.0	0.641	1.20	1.99	2.84	4.66
17.64	0.38	2.0	4.08	8.33	14.9	22.6	40.7
9.72	0.09	2.0	7.93	17.85	34.6	54.6	99.9
8.41	0.19	2.0	8.96	20.1	38.0	59.6	107.0
4.45	0.34	2.0	15.5	35.3	67.0	100.8	171.8

[a] Average deviation for four or more measurements of the pressure.

Table 2

DATA FROM FORCED VAPORIZATION OF CHLOROBENZENE

Pressure (P), mm Hg	Deviation,[a] mm Hg	Temp. (T), °C	Mass Flow (ṅ), μmoles/sec				
			Tube A	Tube B	Tube C	Tube D	Tube E
41.87	0.12	50.0	0	0	0	0	0
39.35	0.13	50.0	0.554	1.01	1.54	2.24	3.62
37.60	0.12	50.0	0.920	1.82	2.64	4.21	6.84
33.14	0.11	50.0	1.92	3.78	6.51	9.60	16.2
28.94	0.05	50.0	2.93	6.01	9.22	15.8	28.5
22.92	0.09	50.0	4.64	10.3	18.4	29.4	56.4
17.54	0.47	50.0	8.10	18.7	32.4	48.3	85.1
13.58	0.19	50.0	14.6	36.5	63.2	98.4	177.5
8.90	0.27	50.0	25.4	70.0	130.1	211.8	174.3
8.89	0.18	50.0	23.2	54.0	102.3	165.9	294.5
8.16	0.5	50.0	33.4	78.0	142.5	202.1	375.4
11.77	0.10	25.0	0	0	0	0	0
10.76	0.15	25.0	0.22	0.47	0.84	0.94	1.50
10.65	0.11	25.0	0.33	0.69	0.94	1.34	2.11
6.86	0.09	25.0	2.83	6.46	7.73	11.7	19.0
6.17	0.10	25.0	4.98	12.8	24.0	38.4	64.9
4.83	0.09	25.0	6.84	17.9	35.5	56.1	97.9
3.58	0.07	25.0	7.90	22.3	43.9	57.6	120.3
3.48	0.20	25.0	8.67	23.4	46.9	75.7	145.1
3.33	0.20	25.0	7.70	20.8	42.3	67.9	124.7
3.03	0.08	25.0	9.20	24.7	49.2	75.8	122.2
3.70	0.09	5.0	0	0	0	0	0
3.38	0.12	5.0	.91	1.85	3.19	4.72	5.62
2.89	0.07	5.0	2.42	6.29	12.3	19.7	14.7
2.83	6.12	5.0	3.62	10.2	20.9	33.2	18.7
2.78	0.16	5.0	3.80	10.4	21.3	32.5	18.7
2.73	0.11	5.0	3.22	8.27	8.53	28.8	50.4

[a]Average deviation for four or more measurements of the pressure.

[b]Flow variance for $\Delta P = \pm 0.1$; 0.1, 0.2, 0.3, 0.4, 0.75 μmoles/sec about 30%.

Table 3

DATA FROM FORCED VAPORIZATION OF BUTANOL

Pressure (P), mm Hg	Deviation,[a] mm Hg	Temp. (T), °C	Mass Flow ($\dot{n}$), μmoles/sec				
			Tube A	Tube B	Tube C	Tube D	Tube E
36.18	1.0	50	0	0	0	0	0
33.5	1.0	50	0.155	0.296	–	0.755	1.24
28.21	0.09	50	0.995	1.916	3.348	4.978	8.550
21.21	0.20	50	2.370	4.805	8.326	12.86	22.01
14.53	0.22	50	3.934	8.237	15.19	22.89	41.92
10.83	0.11	50	5.162	10.90	20.23	32.30	58.78
9.69	0.23	50	5.512	11.85	21.76	34.43	63.16
9.34	0.15	50	5.724	12.02	22.49	36.25	66.90
6.51	0.13	25	0	0	0	0	0
5.72	0.21	25	1.264	2.502	4.335	6.541	10.71
4.67	0.09	25	1.363	2.620	4.473	6.490	11.22
4.97	0.08	25	1.523	2.967	5.080	7.782	13.02
4.43	0.05	25	1.596	3.102	5.283	7.771	13.42
2.29	–	25	3.63	7.42	13.66	21.99	41.81
2.22	0.07	25	3.973	8.323	16.37	26.80	49.70
2.34	0.10	25	4.065	8.350	14.78	26.67	50.15
1.3	–	2	0	0	0	0	0
0.54	0.09	2	0.149	0.252	0.339	0.560	0.966
0.47	–	2	1.06	2.03	3.48	5.26	8.95
0.46	–	2	1.04	2.04	3.48	5.35	9.19

[a] Average deviation for four or more measurements of the pressure.

tetrachloride data are collected appreciably distant from equilibrium (Table 1). Second, there are variations in surface area with vaporization, that is, the meniscus tends to flatten out as steady vaporization rates are increased. This variation of surface area is percentage-wise larger in small tubes relative to large tubes and cross correlation of data for various flow rates is difficult on a specific basis. After unsuccessful attempts to take surface area considerations into account it was decided to handle the data on a specific per-unit-tube area basis. Thus, although the coefficient should be based on the available (varying) surface area within a tube it is henceforth considered on the basis of simple tube area. At infinite tube bore, the surface area approaches the tube area, and a common specific basis is implied. Finally, the profile of density gradients due to surface temperature variations can induce convection effects which effectively short-circuit the relatively pure conduction mode of heat transfer. Because of radial restrictions, the smaller tubes tend to reach a condition of maximum convection at lower flows relative to the larger tubes. Convection effects are generally erratic because they require critical conditions that are dependent on both the equipment geometry and material properties. Certain anomalies that exist in the data are believed due to convection effects.

IV. DATA TREATMENT

The desired objective is indicated by Equation (1), that is, the extrapolated value of a migrational property for the forced vaporization process at equilibrium (zero mass flow) and independent of equipment influence (infinite tube bore). For reasons of mathematical shorthand, the system (z, x, y) is defined by the following equations:

$$z = \dot{n}/A_t \qquad \text{Mass flow per unit tube area.} \qquad (2)$$

$$x = \text{Ln } (P^\circ/P) \qquad \begin{array}{l}\text{Logarithm of pressure ratio} \\ \text{between terminal states.}\end{array} \qquad (3)$$

$$y = 1/r \qquad \begin{array}{l}\text{Reciprocal tube radius, assumed} \\ \text{to define tube geometry.}\end{array} \qquad (4)$$

The data in Tables 1, 2 and 3 are then considered as consistent classes of the sets (z, x, y) for each liquid at the three temperatures that are included.

These data were statistically analyzed in an effort to derive an analytical treatment that achieved the type of results reported[8] with water. Two programs, BMD-02R and BMD-08V, written by the Biomedical Center of the University of California in Los Angeles were used to perform stepwise multiple regression analyses, i.e., the response of regression equation for a particular dependent variable is built up term by term introducing at each step of that term the coefficient which will result in the greatest reduction in the sum of the squared deviations between the observed value of the dependent variable and the values computed by the

by the regression equation. The F values associated with the
coefficient of a term in a regression equation is the square of
the ratio of the coefficient to its standard error (in other
words, the square of the "t" statistic). A multiple correlation
coefficient, R, and the standard deviation of the difference
between the calculated and observed value of the representative
variable being represented in equation form is also reported.

The equation form chosen to represent the correlation is
critical in that the data collected near equilibrium, although
contributing little to the analysis numberically, is most rele-
vant for the desired objective, that is, the slope of z with
respect to x at the unmeasurable conditions of zero mass flow
and reciprocal tube radius. With the values of "F", "R" and i as
indicators of improvements in data correlation, 18 equation forms
were evaluated, the best unified equation being,

$$z = a x + b x y + c x^2 \tag{5}$$

The results of the regression analysis are collected in
Table 4 for the three liquids at the three selected temperatures.
The mean values of z and x, as well as the correlation indices,
are indicated therein. The desired values of the limiting mi-
grational coefficient, N, are also calculated. Values of N
decrease with increasing temperature and probably approach zero
at the critical temperature for particular liquids. Temperature
dependency is shown in Figure 1, where more linear dependencies

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Table 4

ZERO REGRESSION ANALYTICAL COMPUTER FIT
OF FORCED VAPORIZATION DATA FOR THREE LIQUIDS

Liquid	Temperature °C	Equation Constants[1]			Mean Values		Correlation[2]			Vaporization Coefficient N[4]
		A	B	C	x̄[3]	ȳ	F	R	σ	
CCl_4	50.0	.219	1.459	.0365	.08_	.134	14,059.4	.9996	.003	4.57
Cl_4	25.0	.129	1.100	0	.055	.126	762.2	.9909	.011	7.75
CCl_4	2.0	.0638	.747	.101	.383	.934	2,239.9	.9980	.035	15.7
BuOH	50.0	.127	.481	0	.176	.706	13,790.8	.9993	.009	7.87
BuOH	25.0	.115	.415	0	.126	.536	1,007.5	.9907	.022	8.70
BuOh	4.0	.0133	.109	0	.030	.734	37.7	.8984	.020	75.2
C_6H_5Cl	50.0	.543	1.757	0	.668	.737	368.1	.9658	.272	1.04
C_6H_5Cl	25.0	.283	.543	.0563	.348	.729	731.4	.9895	.067	3.53
C_6H_5Cl	2.0	.157	1.334	1.039	.155	.199	101.9	.9586	.059	6.37

[1] $z = A x + B xy + C x^2$

[2] Correlation coefficients from computer regression analysis.

[3] $\dot{w}$ in $\frac{\mu\text{-moles}}{\text{sec-mm}^2}$
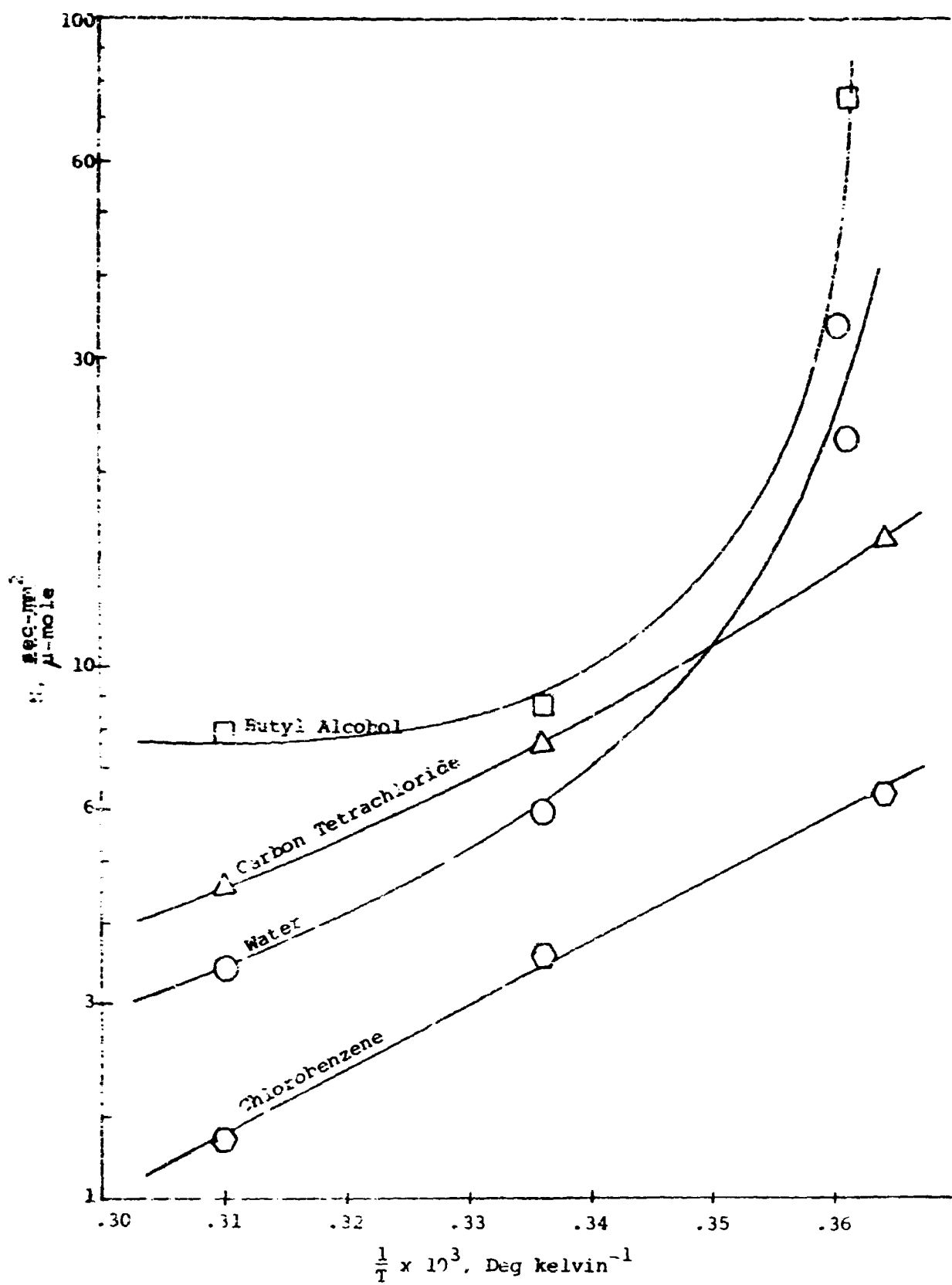
[4] N in $\frac{\text{sec-mm}^2}{\mu\text{-mole}}$

Figure 1

VARIATION OF LIMITING MIGRATIONAL PROPERTY
FOR FOUR LIQUIDS WITH RECIPROCAL ABSOLUTE TEMPERATURE

65   IITRI-C6099-3

are suggested for the non-associated liquids, carbon tetrachloride and chlorobenzen, relative to associated liquids, water and n-butanol.

V. SUMMARY

A new collection of forced vaporization data for three liquids, carbon tetrachloride, chlorobenzene and n-butanol, is presented over broad ranges of pressure, mass flow, tube geometry, and temperature. The data were statistically evaluated in several unified equation formats by a computerized zero regression analysis with the objective of evaluating a limiting value for the migrational coefficient, N.

The equation that resulted in the set of correlation coefficients that indicated the most-improved correlation was found to be,

$$z = a x + b x y + c x^2 \tag{5}$$

Thus, at $x = y = 0$, the desired limit, $\frac{x}{y}$, is simply the reciprocal of a for each data set. Values of N that varied from 1.84 to 75.2 sec-mm^2/μ-mole were found for these liquid systems in the temperature range of approximately 0 to 50°C. Monotonic dependency with temperature was indicated and deviations from a logarithmic linearity were indicated for associated liquids such as n-butanol and water.

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13. ABSTRACT

Interphase transformations have been studied with emphasis on fundametals and their relationship to problems that exist in the explosive sensitivity of liquid propellants. Vaporization and vapor-supply mechanisms play an important role in the sensitivity of condensed-phase propellant systems but their quantitative classification and assessment are difficult to realize.

A pseudo-thermodynamic vaporization coefficient, independent of rate and equipment influence, has been evaluated for water and introduced into the literature. Data for three other liquids, carbon tetrachloride, chlorobenzene and butanol, have been statistically analyzed and results will be published. Consideration of chemical reaction analogs of this treatment was limited.

A mechanism, namely, the fracture of a liquid system under hydrostatic tensile forces is proposed by which liquid systems can vaporize or supply vapor in an explosive fashion. Preliminary verification of this mechanism for liquids in states of negative pressure was obtained and supplemented by related experiments with flashlamp heated gas-black surfaces in contact with both inert and reactive liquids.

The status of the program is reviewed, and a list of accomplishments and publications is given.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Sensitivity						
Vaporization						
Explosive						
Negative pressure						
Cohesive-adhesive foces						
Interphase transformations						
Chemical reaction						
Vapor-supply mechanism						